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TITLE: COMPOSITION MEASURING METHOD FOR BUFFERED HYDROFLUORIC ACID FOR SEMICONDUCTOR  
WAFER ETCHING

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## ABSTRACT:

PURPOSE: To precisely estimate composition by finding respective composition ratios from physical property values (including density itself) and refraction factor proportional to the density of buffered hydrofluoric acid for semiconductor wafer etching.

CONSTITUTION: Semiconductor wafer etching liquid EQ composed of mixed aqueous solution of ammonium fluoride density 10-30wt.% and hydrogen fluoride density 0.5-10wt.% is circulated from an etching tank via a pump and a constant temperature vessel, the refraction factor and purge back pressure are measured in time series or continuously by a refractometer and a purge back pressure measuring device so as to be converted into current signals and inputted to a computer system via an interface. A composition ratio estimation equation based on simultaneous equations (an equation I, an equation II, an equation III) determining coefficients and absolute terms proportional to the composition ratio is programmed beforehand in a computer system so that the input value is processed thereby and the composition ratio of an etching wave is calculated.

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TITLE: COMPOSITION MEASURING METHOD FOR BUFFERED HYDROFLUORIC ACID FOR SEMICONDUCTOR  
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(54)【発明の名称】 半導体ウエハエッチング用バッファードフッ酸の組成測定方法

(57)【要約】

【目的】 バッファードフッ酸の組成分率をリアルタイムで測定可能にし、エッチング工程を管理するに好適なバッファードフッ酸の組成測定方法を提供する。

【構成】 フッ化アンモニウム濃度が10～30wt %、フッ化水素濃度が0.5～10wt %である混合水溶液からなる半導体ウエハエッチング用バッファードフッ酸の密度と比例する物性値及び屈折率を測定し、本発明の連立方程式に基づき各成分の組成分率を算出するようにした。

## 【特許請求の範囲】

【請求項1】 フッ化アンモニウム濃度が10～30wt%、フッ化水素濃度が0.5～10wt%である混合水溶液からなる半導体ウエハエッチング用バッファードフッ酸の密度と比例する物性値及び屈折率を測定し、下記の(1a)、(1b)、(1c)式からなる連立方程式に基づき各成分の組成分率を算出する半導体ウエハエッチング用バッファードフッ酸の組成測定方法。

$$n_D = a_1 x_1 + b_1 x_2 + c_1 x_3 \quad \dots (1a)$$

$$d = a_2 x_1 + b_2 x_2 + c_2 x_3 \quad \dots (1b)$$

$$1 = x_1 + x_2 + x_3 \quad \dots (1c)$$

但し、式中、

$x_1$ はフッ化水素の組成分率、

$x_2$ はフッ化アンモニウムの組成分率、

$x_3$ は水の組成分率、

$n_D$ は屈折率

$a_1$ 、 $b_1$ 、 $c_1$ はそれぞれの組成分率の屈折率の係数、

$d$ は密度と比例する物性値、

$a_2$ 、 $b_2$ 、 $c_2$ はそれぞれの組成分率の密度と比例する物性値の係数を表す。

【請求項2】 前記密度と比例する物性値 $d$ が、バッファードフッ酸中の定深さで一定圧力の窒素ガスをバージした際のバージ背圧である請求項1記載の半導体ウエハエッチング用バッファードフッ酸の組成測定方法。

【請求項3】 前記密度と比例する物性値 $d$ が、密度自体である請求項1記載の半導体ウエハエッチング用バッファードフッ酸の組成測定方法。

## 【発明の詳細な説明】

## 【0001】

## 【産業上の利用分野】

【0002】本発明は、バッファードフッ酸の組成測定方法に関し、特に、半導体ウエハのエッチング液として使用されるフッ化水素、フッ化アンモニウム及び水からなるバッファードフッ酸中のフッ化水素濃度を制御して、エッチング工程を管理するに好適な半導体ウエハエッチング用バッファードフッ酸の組成測定方法に関するものである。

## 【0003】

【従来の技術】半導体ウエハのエッチングにおいて、フッ酸、バッファードフッ酸等のフッ化水素系の薬品を使用する場合、その組成、特にフッ化水素濃度はエッチング速度に大きく影響を及ぼすことから、その濃度を厳しく管理する必要がある。ところが、エッチング工程におけるインライン型の濃度モニターを採用しようとした場合は、金属、ダスト等による汚染がなく、測定精度、感度、応答速度等も充足しなければならず、工業的に十分に満足できるものがなかった。このような理由から、従来は、濃度の保証された薬品が市販されており、これを購入して用いるようにしているが、その場合、ウエハ処理工程によってエッチングプロセスの条件が異なるた

め、濃度の異なる多種類の薬品を保管管理しなければならなかった。

【0004】なお、三成分系混合液の分析方法として、特公平4-64576号には、屈折率と比重とを測定しこれを基にして成分組成を算出する方法が記載されており、実施例として、メタクリロイルオキシエチルトリメチルアンモニウムクロライド、アクリルアミド及び水の三成分系溶液にこの方法が適用されている。また、特開平6-273306号には、前記方法の統計的処理の改良法が記載されており、三成分系溶液において物性に加成性がある場合、二種の物性を測定し、統計的手法により組成を算出することが可能であることは知られている。しかしながら、どのような成分の物性に加成性があるか、また、どの濃度範囲に加成性があるかなどについて解明されていないことが多く、半導体ウエハエッチング用のバッファードフッ酸中のフッ化水素濃度についても同様である。

## 【0005】

【発明が解決しようとする課題】したがって、バッファードフッ酸を使用したシリコン酸化膜のエッチングにおいては、その液組成がエッチング速度に直ちに影響を及ぼすためその液組成を容易に把握しエッチング条件にリアルタイムに反映したり管理することが切望されているものの、未だ十分満足できる方法がなく、前述の如く濃度保証された多種類の薬品を予め保管して用いなければならず、ランニングコスト増などが問題となっている。なお、バッファードフッ酸によるシリコン酸化膜のエッチングでは、フッ化アンモニウム濃度10～30wt%の範囲において、エッチング速度はフッ化水素濃度に専ら依存し、フッ化アンモニウム濃度の影響は少ないことが分かっており、仮に、フッ化水素濃度をリアルタイムに知ることが可能になればエッチング管理上、極めて有用なものとなる。

【0006】そこで、本発明者らは、フッ化水素とフッ化アンモニウムとの混合水溶液の組成測定方法について種々検討してきた結果、シリコン酸化膜のエッチング剤として極めて好ましい濃度範囲内において、混合溶液の密度と比例する物性値及び屈折率から、精度良くその組成を推算することが可能であることを見出し、本発明を完成するに至った。

## 【0007】

【課題を解決するための手段】すなわち、本発明に係るバッファードフッ酸の組成測定方法は、フッ化アンモニウム濃度が10～30wt%、フッ化水素濃度が0.5～10wt%である混合水溶液からなる半導体ウエハエッチング用バッファードフッ酸の密度と比例する物性値（密度自体を含む）及び屈折率を測定し、その値から各成分の組成分率を下記の連立方程式により算出するものである。

【0008】フッ化水素0.5～10wt%以下、フッ

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化アンモニウム濃度10～30wt%及び水からなる三成分系溶液においては、密度と比例する物性値（密度自\*

\*体を含む）及び屈折率に加成性があり、次の（1a）、（1b）、（1c）式からなる連立方程式が成立する。

$$n_D = a_1 x_1 + b_1 x_2 + c_1 x_3 \quad \dots (1a)$$

$$d = a_2 x_1 + b_2 x_2 + c_2 x_3 \quad \dots (1b)$$

$$1 = x_1 + x_2 + x_3 \quad \dots (1c)$$

但し、式中、 $x_1$ はフッ化水素の組成分率、 $x_2$ はフッ化アンモニウムの組成分率、 $x_3$ は水の組成分率、 $n_D$ は屈折率

※る物性値としては、密度の他、密度よりも容易に測定可能なパーシ背圧などが挙げられる。

【作用】

$a_1$ 、 $b_1$ 、 $c_1$ はそれぞれの組成分率の屈折率の係数、 $d$ は密度と比例する物性値（密度自体も含む）、 $a_2$ 、 $b_2$ 、 $c_2$ はそれぞれの組成分率の密度と比例する物性値の係数を表す。なお、本発明において、前記 $d$ で表され※

【0009】前記（1a）～（1c）式からなる第1の連立方程式から、次の（2a）、（2b）式からなる第2の連立方程式が導かれる。

$$n_D = (a_1 - c_1) x_1 + (b_1 - c_1) x_2 + c_1 \quad \dots (2a)$$

$$d = (a_2 - c_2) x_1 + (b_2 - c_2) x_2 + c_2 \quad \dots (2b)$$

【0010】ここで、前記 $a_1$ 、 $b_1$ 、 $c_1$ 及び前記 $a_2$ 、 $b_2$ 、 $c_2$ は一定の温度で固有の定数であり、組成分率が既知の多数のサンプルの屈折率 $n_D$ 及び密度と比例する物性値 $d$ を測定し、これらのデータを前記（1a）～（1c）式あるいは（2a）及び（2b）式に当てはめ、通常の統計的手法で処理することにより、上記の連立方程式が決まる。したがって、組成分率未知の混合溶液の屈折 $n_D$ 及び密度と比例する物性値 $d$ を測定し、前記（1a）～（1c）からなる第1の連立方程式又は前記（2a）、（2b）からなる第2の連立方程式を解けば各組成分率を算出することができる。その際には、当然、前記各連立方程式の係数及び定数項の決定にあたって、採用した測定温度と、実際の組成分率測定の際の温度は一致させる必要がある。

★いる。この循環するエッチング液EQは、恒温器3からエッチング槽1の間の配管部に接続された屈折計4及びパーシ背圧測定器5により時系列ないしは連続的に屈折率及びパーシ背圧が計測される。

【0011】本発明において、使用する屈折計にあっては、フッ酸の屈折率が水よりも小さいため、特殊なプリズムを使用する必要がある。また、プリズムの材質は一般のソーダガラスではフッ酸に侵されるので、サファイア等のフッ酸耐性の材質を使用する必要がある。このような屈折計としては、半導体薬品用として実用化されているものを使用できる。密度と比例する物性値 $d$ としては、密度又は比重をフッ酸耐性の浮秤等による比重測定しても良いが、より簡易にはバッファードフッ酸中の一定深さで一定圧力の不活性ガス、例えば窒素ガスをパーシし、その背圧（パーシ背圧）を測定する方法が好ましい。この種の分析装置としては、半導体製造プロセスにおいて液面計として実用化されているものが使用可能である。

【0014】前記パーシ背圧測定器5は、図2に示す如く窒素ガスが使用されており、窒素ガスがガス供給部6の流量調整バルブで流量を制御されてフィルター7から検出パイプ部8を経由して、測定用として導出されたエッチング液部9の一定液深にパーシされる。検出パイプ部8は液面計ないしはパーシ背圧検知計10に接続されており、パーシ背圧が計測される。

【0012】

【実施例】以下、実施例により本発明を更に詳細に説明する。図1は半導体のエッチング工程におけるエッチング液の組成管理システムを示すブロック図、図2は前記システムに用いられたパーシ背圧測定器の計測原理を示すブロック図である。

【0015】そして、屈折計4及びパーシ背圧測定器5により計測された各計測値は、電流信号に変換されてインターフェイス11を介してコンピューターシステム12に入力される。コンピューターシステム12には、予め係数及び定数項を定めた前記式（2a）、（2b）からなる第2の連立方程式に基づく組成分率推算式がプログラムされており、これによって入力値が処理されエッチング液の組成分率が演算されて表示部（図示しない）に表示されたり、プリンターされる。

【0013】エッチング槽1内のエッチング液EQは、図1に示す如くポンプ2、恒温器3を介して循環されて★50

【0016】更に、図1の組成管理システムでは、調整用のフッ酸供給部13とフッ化アンモニウム水溶液供給部14とが設けられ、前記コンピューターシステム7からの指令により各供給部13、14の流量調整バルブ（図示しない）が作動制御されて、エッチング槽1内のエッチング液EQについてその組成が一定に保たれるようになっている。

【0017】（実施例1）49.9wt%のフッ酸、40.4wt%のフッ化アンモニウム水溶液及び純粋を混合し、フッ化水素濃度1～6wt%、フッ化アンモニウム濃度10～30wt%の範囲で54種（フッ化水素1、2、3、4、5、6wt%、フッ化アンモニウム10、12、14、16、18、20、22、24、26wt%）の組成のバッファードフッ酸を調整し、液温20℃におけるそれぞれの屈折率とパーシ背圧（混合液中の一定の深さで窒素ガスをパーシし、その背圧mmH<sub>2</sub>

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O)を測定し、重回帰分析の手法により、このデータを前記(2a)、(2b)からなる第2の連立方程式に当て

\*てはめて処理し、下記の推算式(3a)、(3b)を得

$$n_D = 0.00074x_1 - 0.00151x_2 + 1.33767 \quad \dots (3a)$$

$$d = 1.56250x_1 + 0.87937x_2 + 490.22315 \quad \dots (3b)$$

この推算式(3a)、(3b)の精度を調べるため、屈折率の実測値 $n_D$ と、密度と比例する物性値 $d$ (パージ背圧mmH<sub>2</sub>O)の実測値とを推算式(3a)、(3b)に代入して組成分率の推算値を求めた。その結果は、下記の通り、誤差の相対標準偏差を求めたところ、フッ化アンモニウムで0.019、フッ化水素で0.113となり、実用的に十分な精度であることが確認された。

相対誤差CV = (設定値 - 推算値) / 設定値

相対標準偏差 =  $\{\sum (CV)^2 / (n-1)\}^{1/2}$

但し、n: サンプル数

【0018】(参考比較例)フッ化アンモニウム0~40wt%、フッ化水素0~6wt%の範囲の136種のサンプルを用い、実施例と同様に推算式を求め、誤算の相対標準偏差を計算したところ、フッ化アンモニウムで0.584、フッ化水素で0.205と、実施例に比べ大きな誤差となった。

※【0019】

【発明の効果】以上の本発明によれば、バッファードフッ酸の組成分率をリアルタイムで高性能に測定できる。これにより、従来のように多種の濃度保証された薬液を保管する必要がなくなり、エッチング工程をより正確かつ容易に管理することが可能となる。

【図面の簡単な説明】

【図1】本発明を適用した半導体のエッチング工程におけるエッチング液の組成管理システムを示すブロック図である。

【図2】前記組成管理システム中の背圧測定器を示すブロック図である。

【符号の説明】

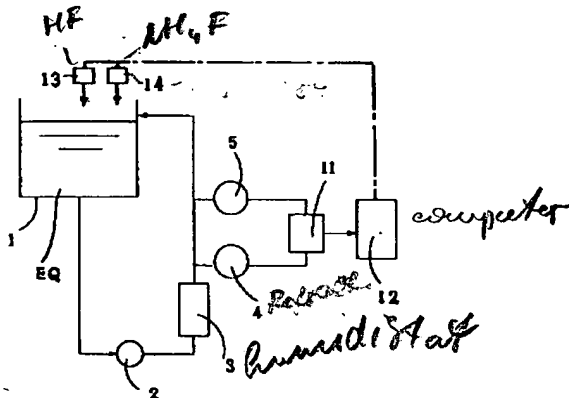
1 エッチング槽

4 屈折計

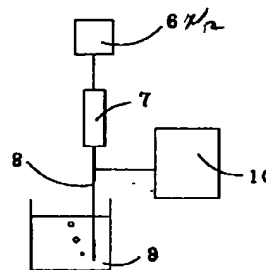
5 背圧測定器

※ 12 コンピュータシステム

【図1】



【図2】



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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

## [Industrial Application]

[0002] Especially this invention relates to the composition measuring method of the suitable buffered fluoric acid for semiconductor wafer etching to control the hydrogen fluoride concentration in the buffered fluoric acid which consists of the hydrogen fluoride, the ammonium fluoride, and water which are used as an etching reagent of a semiconductor wafer about the composition measuring method of buffered fluoric acid, and manage an etching process.

[0003]

[Description of the Prior Art] In etching of a semiconductor wafer, when using the chemical of hydrogen fluoride systems, such as fluoric acid and buffered fluoric acid, since the composition, especially hydrogen fluoride concentration affect an etch rate greatly, they need to manage the concentration severely. However, when it was going to employ the concentration monitor of the inline type in an etching process, there was no contamination by the metal, dust, etc., and the accuracy of measurement, sensitivity, the speed of response, etc. had to be satisfied, and there was nothing that can fully be satisfied industrially. Since it was such, although the chemical with which concentration was guaranteed is marketed, and it purchases this and is made to use conventionally, since the conditions of an etching process changed with wafer down stream processing in that case, storage management of the chemical of varieties with which concentration differs had to be carried out.

[0004] In addition, the method of measuring a refractive index and specific gravity and computing component composition based on this is indicated by JP,4-64576,B as analytical method of three-component-system mixed liquor, and this method is applied to methacryloxy-ethyl trimethylammonium chloride, the acrylamide, and the three-component-system solution of water as an example. Moreover, when the method of improving the statistical procedure of the aforementioned method is indicated and additive property is in physical properties in a three-component-system solution, two sorts of physical properties are measured to JP,6-273306,A, and it is known that it is possible to compute composition by the statistical method. However, it is not solved in many cases about whether additive property is in the physical properties of what component, and in which density range additive property is, and the same is said of the hydrogen fluoride concentration in the buffered fluoric acid for semiconductor wafer etching.

[0005]

[Problem(s) to be Solved by the Invention] Therefore, if the chemical of the varieties by which there is no method of still satisfying enough although it is anxious for grasping the liquid composition easily in order that the liquid composition may affect an etch rate immediately in etching of the silicon oxide which used buffered fluoric acid, and it being reflected in etching conditions on real time, or managing, and the concentration guarantee was offered like the above-mentioned is kept beforehand, it does not use and it is an oak, the increase of \*\* and a running cost etc. poses a problem. In addition, in the range of ammonium-fluoride concentration 10 - 30wt%, chiefly depending on hydrogen fluoride concentration, <<

the etch rate understands that the influence of ammonium-fluoride concentration is few, and by etching of the silicon oxide by buffered fluoric acid, temporarily, if it becomes possible to get to know hydrogen fluoride concentration on real time, it will become very useful on etching management.

[0006] Then, as a result of having examined many things about the composition measuring method of the mixed-water solution of hydrogen fluoride and an ammonium fluoride, this invention persons find out that it is possible to guess the composition with a sufficient precision from the physical-properties value which is proportional to the density of a mixed solution at concentration within the limits very desirable as an etching agent of a silicon oxide, and a refractive index, and came to complete this invention.

[0007]

[Means for Solving the Problem] That is, ammonium-fluoride concentration measures the physical-properties value (the density itself is included) and refractive index proportional to the density of the buffered fluoric acid for semiconductor wafer etching which hydrogen fluoride concentration becomes from the mixed-water solution which is 0.5 - 10wt% 10 - 30wt%, and the composition measuring method of the buffered fluoric acid concerning this invention computes composition separation of each component by the following simultaneous equations from the value.

[0008] In the three-component-system solution which consists of less than [ hydrogen fluoride 0.5-10wt% ], ammonium-fluoride concentration 10 - 30wt% and water, additive property is in the physical-properties value (the density itself is included) and refractive index proportional to density, and the simultaneous equations which consist of the following (1a), (1b), and a formula (1c) are materialized.

$$nD = a_1x_1 + b_1x_2 + c_1x_3 \dots (1a)$$

$$d = a_2x_1 + b_2x_2 + c_2x_3 \dots (1b)$$

$$1 = X_1 + X_2 + X_3 \dots (1c)$$

The composition molar fraction of hydrogen fluoride and  $x_2$  among a formula  $x_1$  However, the composition molar fraction of an ammonium fluoride, The physical-properties value (the density itself is included) to which in the composition molar fraction of water and  $nD$  refractive indexes  $a_1$ ,  $b_1$ , and  $c_1$  are proportional to the coefficient of the refractive index of each composition molar fraction, and  $d$  is [  $x_3$  ] proportional to density, and  $a_2$ ,  $b_2$  and  $c_2$  express the coefficient of the physical-properties value proportional to the density of each composition molar fraction. In addition, in this invention, measurable purge back pressure etc. is mentioned as a physical-properties value expressed with Above  $d$  more easily than density besides density.

[Function]

[0009] From the 1st simultaneous equations which consist of the above (1a) - (1c) a formula, the 2nd simultaneous equations which consist of the following (2a) and a formula (2b) are drawn.

$$nD = (a_1 - c_1)x_1 + (b_1 - c_1)x_2 + c_1 \dots (2a)$$

$$d = (a_2 - c_2)x_1 + (b_2 - c_2)x_2 + c_2 \dots (2b)$$

[0010] The above  $a_1$ ,  $b_1$ , and  $c_1$  and the above  $a_2$ ,  $b_2$ , and  $c_2$  are peculiar constants at fixed temperature here. the physical-properties value  $d$  to which a composition molar fraction is proportional to the refractive index  $nD$  of many known samples, and density -- measuring -- these data -- the above (1a) - (1c) a formula -- or (2a) -- and (2b) the above-mentioned simultaneous equations are decided by applying to a formula and processing by the usual statistical method Therefore, the physical-properties value  $d$  proportional to Refraction  $nD$  and density of the mixed solution of composition molar-fraction strangeness is measured, and if the 1st simultaneous equations or the above (2a) which consists of aforementioned (1a) - (1c), and the 2nd simultaneous equations which consist of (2b) are solved, the rate of a class component is computable. Naturally it is necessary in the coefficient of each aforementioned simultaneous equations, and the determination of a constant term to make in agreement the adopted measurement temperature and the temperature in the case of actual composition molar-fraction measurement in that case.

[0011] In this invention, if it is in the refractometer to be used, since the refractive index of fluoric acid is smaller than water, it is necessary to use special prism. Moreover, since the quality of the material of prism is invaded by fluoric acid by the general soda glass, it is necessary to use the quality of the



material of fluoric acid resistance, such as sapphire. As such a refractometer, what is put in practical use as an object for semiconductor chemicals can be used. As a physical-properties value  $d$  proportional to density, although a hydrometry may be carried out, the method of purging more simply the inert gas of a constant pressure, for example, nitrogen gas, in the fixed depth in buffered fluoric acid, and measuring the back pressure (purge back pressure) according to density or specific gravity to the hydrostatic balance of fluoric acid resistance etc. is desirable. What is put in practical use as a level gage in the semiconductor manufacture process as this kind of an analysis apparatus is usable.

[0012]

[Example] Hereafter, an example explains this invention still in detail. The block diagram showing the composition managerial system of an etching reagent [ in / the etching process of a semiconductor / in drawing 1 ] and drawing 2 are the block diagrams showing the measurement principle of the purge back pressure measuring instrument used for the aforementioned system.

[0013] As shown in drawing 1, it circulates through the etching reagent EQ in the etching tub 1 through the pump 2 and the humidistat 3. Time series or a per-continuum refractive index, and purge back pressure are measured by the refractometer 4 and the purge back pressure measuring instrument 5 by which this etching reagent EQ through which it circulates was connected to the piping section between the etching tubs 1 from the humidistat 3.

[0014] As shown in drawing 2, nitrogen gas is used, and the aforementioned purge back pressure measuring instrument 5 is purged by the fixed depth of the etching-reagent section 9 by which nitrogen gas had the flow rate controlled by the flow control bulb of the gas supply section 6, and was drawn from the filter 7 as an object for measurement via the detection pipe section 8. The detection pipe section 8 is connected to a level gage or purge back pressure detection 10 [ a total of ], and purge back pressure is measured.

[0015] And each measurement value measured by the refractometer 4 and the purge back pressure measuring instrument 5 is changed into a current signal, and is inputted into a electronic computing system 12 through an interface 11. The composition molar-fraction guess formula based on the aforementioned formula (2a) which defined the coefficient and the constant term beforehand, and the 2nd simultaneous equations which consist of (2b) is programmed by the electronic computing system 12, an input value is processed, the composition molar fraction of an etching reagent calculates, it is displayed on a display (not shown) or a printer is carried out to it by this.

[0016] Furthermore, in the composition managerial system of drawing 1, the fluoric acid feed zone 13 and the ammonium-fluoride solution feed zone 14 for adjustment are prepared, operation control of the flow control bulb (not shown) of each feed zones 13 and 14 is carried out by the instructions from the aforementioned electronic computing system 7, and the composition is kept constant about the etching reagent EQ in the etching tub 1.

[0017] A 49.9wt% fluoric acid, 40.4wt% ammonium-fluoride solution, and purity are mixed. (Example 1) the range of hydrogen fluoride concentration 1 - 6wt% and ammonium-fluoride concentration 10 - 30wt% -- 54 sorts (hydrogen fluoride 1, 2, 3, 4, and 5 and 6wt% --) Ammonium fluorides 10, 12, 14, 16, 18, 20, 22, and 24 and the buffered fluoric acid of 26wt% of composition are adjusted. Each refractive index and purge back pressure (nitrogen gas is purged in the fixed depth in mixed liquor, and it is back pressure mmH<sub>2</sub>O) in 20 degrees C of solution temperature are measured. by the technique of a multiple regression analysis This data was applied to the above (2a) and the 2nd simultaneous equations which consist of (2b), and was processed, and the following guess formula (3a) and (3b) were obtained.  $nD = 0.00074x_1 - 0.00151 x_2 + 1.33767 \dots$  (3a)

$d = 1.56250x_1 + 0.87937 x_2 + 490.22315 \dots$  (3b)

In order to investigate this guess formula (3a) and the precision of (3b), the fruit side value  $nD$  of a refractive index and the actual measurement of the physical-properties value  $d$  proportional to density (purge back pressure mmH<sub>2</sub>O) were substituted for a guess formula (3a) and (3b), and the guess value of a composition molar fraction was calculated. When the result asked for relative standard deviation with error as follows, it was set to 0.019 by the ammonium fluoride, and was set to 0.113 with hydrogen fluoride, and it was checked that it is sufficient precision practical.

Set-point relative-standard-deviation = [ relative error valve flow coefficient = (set point-guess value) / ]  
 $\{\sigma(\text{valve-flow-coefficient})^2 / (n-1)\}^{1/2}$ , however n: Measurement size [0018] (Example of reference comparison) When it asked for the guess formula like the example and the relative standard deviation of miscalculation was calculated ammonium-fluoride 0 - 40wt% using 136 sorts of samples of the range of hydrogen fluoride 0 - 6wt%, it compared with 0.584 by the ammonium fluoride, compared with 0.205 and the example with hydrogen fluoride, and became gross errors.

[0019]

[Effect of the Invention] According to the above this invention, the composition molar fraction of buffered fluoric acid can be measured highly efficiently on real time. It becomes possible for it to become unnecessary to keep the medical fluid with which the concentration guarantee of the variety was offered like before by this, and to manage an etching process more correctly and easily.

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[Translation done.]

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the block diagram showing the composition managerial system of the etching reagent in the etching process of the semiconductor which applied this invention.

[Drawing 2] It is the block diagram showing the back pressure measuring instrument in the aforementioned composition managerial system.

[Description of Notations]

- 1 Etching Tub
- 4 Refractometer
- 5 Back Pressure Measuring Instrument
- 12 Computer System

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[Translation done.]

## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : NISSO ENG KK

(22)Date of filing : 07.06.1995

(72)Inventor : KOBAYASHI NORIYUKI

## (54) COMPOSITION MEASURING METHOD FOR BUFFERED HYDROFLUORIC ACID FOR SEMICONDUCTOR WAFER ETCHING

## (57)Abstract:

PURPOSE: To precisely estimate composition by finding respective composition ratios from physical property values (including density itself) and refraction factor proportional to the density of buffered hydrofluoric acid for semiconductor wafer etching.

CONSTITUTION: Semiconductor wafer etching liquid EQ composed of mixed aqueous solution of ammonium fluoride density 10-30wt.% and hydrogen fluoride density 0.5-10wt.% is circulated from an etching tank via a pump and a constant temperature vessel, the refraction factor and purge back pressure are measured in time series or continuously by a refractometer and a purge back pressure measuring device so as to be converted into current signals and inputted to a computer system via an interface. A composition ratio estimation equation based on simultaneous equations (an equation I, an equation II, an equation III) determining coefficients and absolute terms proportional to the composition ratio is programmed beforehand in a computer system so that the input value is processed thereby and the composition ratio of an etching wave is calculated.

$$C_1 = a_1 x_1 + b_1 x_2 + c_1 x_3 \quad \text{I}$$

$$C_2 = a_2 x_1 + b_2 x_2 + c_2 x_3 \quad \text{II}$$

$$1 = x_1 + x_2 + x_3 \quad \text{III}$$

但し、式中、

 $x_1$  はフッ化水素の組成分率、 $x_2$  はアンモニウムフッ化水素の組成分率、 $x_3$  は水の組成分率、 $a_1, b_1, c_1$  は定数、 $a_2, b_2, c_2$  はそれぞれ組成分率の低次元の係数、 $C_1, C_2$  は密度と比例する物理量、 $a_1, b_1, c_1$  はそれぞれ組成分率の定数と比例する物理量の係数を表す。

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JAPANESE

[JP,08-334461,A]

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE  
INVENTION TECHNICAL PROBLEM MEANS OPERATION EXAMPLE DESCRIPTION OF  
DRAWINGS DRAWINGS

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[Translation done.]

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## CLAIMS

[Claim(s)]

[Claim 1] The composition measuring method of the buffered fluoric acid for semiconductor wafer etching which measures the physical-properties value and refractive index proportional to the density of the buffered fluoric acid for semiconductor wafer etching which consists of a mixed-water solution whose hydrogen fluoride concentration ammonium-fluoride concentration is 10 - 30wt%, and is 0.5 - 10wt%, and computes the composition molar fraction of each component based on the simultaneous equations which consist of the following (1a), (1b), and a formula (1c).

$$nD = a_1x_1 + b_1x_2 + c_1x_3 \dots (1a)$$

$$d = a_2x_1 + b_2x_2 + c_2x_3 \dots (1b)$$

$$1 = X_1 + X_2 + X_3 \dots (1c)$$

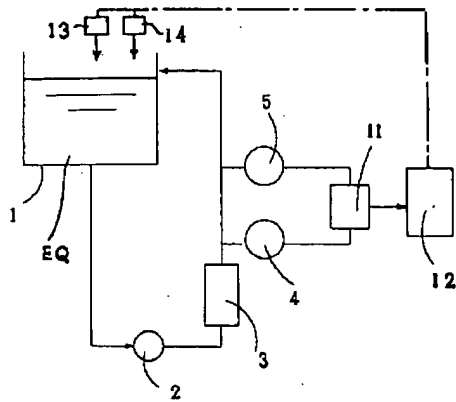

However, the coefficient of the physical-properties value to which  $x_1$  is proportional to the physical-properties value to which in the composition molar fraction of water and  $nD$  refractive indexes  $a_1$ ,  $b_1$ , and  $c_1$  are proportional to the coefficient of the refractive index of each composition molar fraction, and  $d$  is [ the composition molar fraction of hydrogen fluoride and  $x_2$  / the composition molar fraction of an ammonium fluoride and  $x_3$  ] proportional to density among a formula, and  $a_2$ ,  $b_2$ , and  $c_2$  are proportional to the density of each composition molar fraction is

[Claim 2] The composition measuring method of the buffered fluoric acid for semiconductor wafer etching according to claim 1 which is the purge back pressure at the time of the physical-properties value  $d$  proportional to the aforementioned density purging the nitrogen gas of a constant pressure in the constant depth in buffered fluoric acid.

[Claim 3] The composition measuring method of the buffered fluoric acid for semiconductor wafer etching according to claim 1 whose physical-properties value  $d$  proportional to the aforementioned density is the density itself.

[Translation done.]



Drawing selection drawing 1 

[Translation done.]

**JAPANESE** [JP,08-334461,A]

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE  
INVENTION TECHNICAL PROBLEM MEANS OPERATION EXAMPLE DESCRIPTION OF  
DRAWINGS DRAWINGS

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[Translation done.]

JAPANESE

[JP,08-334461,A]

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE  
INVENTION TECHNICAL PROBLEM MEANS OPERATION EXAMPLE DESCRIPTION OF  
DRAWINGS DRAWINGS

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[Translation done.]